PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference Cal 88149	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/EP2004/006932	International filing date *(day/month/year)* 25.06.2004	Priority date *(day/month/year)* 03.07.2003

International Patent Classification (IPC) or national classification and IPC
B01J27/16, B01J27/182, B01J35/10, B01J37/03, C10G49/06

Applicant
ENI S.P.A.

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 12 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
25.01.2005	29.09.2005

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/006932

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-3, 5, 6, 8-10, 12-19, 21, 22, 24-41	as originally filed
4, 4a, 7, 11, 20, 23	received on 06.05.2005 with letter of 03.05.2005

Claims, Numbers

1-27	received on 06.05.2005 with letter of 03.05.2005

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	4-10,15-27
	No:	Claims	1-3,11-14
Inventive step (IS)	Yes:	Claims	15-22
	No:	Claims	4-10,23-27
Industrial applicability (IA)	Yes:	Claims	1-27
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:
   D1: EP-A-0 529 923
   D2: EP-A-0 748 652

2. The present application does not meet the requirements of Article 33(1) PCT, because the subject-matter of claims 1-14 and 23-27 is not new in the sense of Article 33(2) PCT or does not involve an inventive step in the sense of Article 33(3) PCT in view of at least one of the documents D1 to D2.

   In his letter of reply, the applicant argues that the claimed catalytically active amorphous porous solid differs in a substantial way from the solid disclosed in D1, because it consists of an amorphous mixed oxide of Si, Al and P, while the solid of D1 consists of a "solid solution" of different oxides.

   It is pointed out that the process of preparation is not recited in independent claim 1; the terms "mixed oxide" and "solid solution" are considered to be equivalent. Besides, an unclear term cannot be used to render the subject-matter novel over the prior art.

2.1 The subject-matter of independent claims 1 and 11 is anticipated by D1, see claims 1, 2, 9 and 10. The end points of the ranges are specifically disclosed; 90 wt% SiO_2, 5 wt% P_2O_5 and 5 wt% Al_2O_3 gives a composition with Si/Al=15, P/Al= 0.7; the skilled person would seriously contemplate working with pore volumes in the range of overlap (see examples).

   Dependent claims 2-10 and 12-14 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty (Article 33(2) PCT), or are associated with any unexpected technical effect that could support an inventive step (Article 33(3) PCT).

2.2 The solution provided in claims 23-27 is obvious for the skilled person, as soon as the problem underlying them is formulated in view of D1. Hence, no inventive step can be recognised for the subject-matter of claims 23-27.

2.3 The subject-matter of claims 15-22 appears to be allowable under Article 33(1) PCT in view of the available prior art documents.

The subject-matter of independent claim 15 mainly differs from D2 in that an aqueous mixture is prepared which is heated in an alkaline environment without exchange of material with the outside, in different ratios than in D2. In D2, a solution, in an alcohol, of $Al(OR)_3$, and possibly a source of one or more elements selected from Si, B, P and/or group VIII, is subjected to hydrolysis at temperatures between 20 to 80°C with water containing R_4N-OH and possibly a compound of group VIB.

The subject-matter of claim 15 is a non-obvious solution for the problem of the provision of a process for the preparation of the amorphous porous solid as defined in claim 1.

lysts in oligomerization reactions.

Wide literature is also available on molecular sieves based on silica and alumina additionally comprising a phosphorus compound (so-called SAPO®). US patent 4,859,311, for example, describes molecular sieves consisting of silico-alumino-phosphates having a microporous structure with an average pore diameter ranging from 0.3 to 0.7 nm, on which one or more metals with a hydro-dehydrogenating activity, used for removing waxy components of certain paraffinic mixtures (catalytic dewaxing), are deposited. These compositions, however, do not seem to be entirely satisfactory as catalysts in integrated processes for the production of lubricating bases and medium distillates from high-boiling linear paraffinic fractions.

According to European patent EP 492,697, a catalytic composition is described, consisting of an amorphous porous solid comprising silica and at least one oxide of a second metal having a catalytic activity selected from Ti, Ga, Cr, Fe, Zr, V, Mo, Zn, Co, P and Sn. Although this matrix of oxides has various uses as acidic or oxidation catalyst, it does not contain aluminum and is consequently not satisfactory as an active carrier for the hydrogenating and isomerization treatment of paraffinic mixtures. INSERT PAGE 4A

US patents 5,230,789 and 5,139,989 describes certain particular catalytic compositions consisting of amorphous solid solutions

EP 748652 discloses a semi-crystalline solid based on alumina and variable amounts of other metal oxides like Ni or Mo, particularly useful as catalyst in the hydrodesulfurization of fuel oils. A low amount of phosphoric oxide may also be included in the solid.

vantageous characteristics, both when used as such in acid-catalyzed and oligomerization processes, and also as active catalyst carrier in refining processes such as the hydrotreatment of hydrocarbons for the production of fuels and bases for lubricating oils.

A first object of the present invention therefore relates to an amorphous porous solid, catalytically active, comprising a mixed oxide of silicon, aluminum and phosphorus, characterized by an Si/Al atomic ratio ranging from 10 to 250, a P/Al ratio of at least 0.1, ~~, but lower than 5~~ and not higher than 3.5, preferably ranging from 0.3 to 3.5, a total pore volume ranging from 0.5 to 2.0 ml/g, with an average pore diameter ranging from 3 nm to 40 nm, and a specific surface area ranging from 200 to 1000 m^2/g, preferably from 300 to 900 m^2/g.

A second object of the present invention relates to an original process for the preparation of said amorphous porous solid by means of the sol/gel technique starting from Si and Al alkoxides and at least one phosphorus compound suitable for the purpose.

Other objects of the present invention will appear evident from the following description and claims.

The term amorphous as used herein with reference to the porous solid of the present invention and its compositions and uses, indicates a substantial absence of low an-

gel methods for the preparation of micro- or meso-porous amorphous silico-alumina, by the addition of a suitable quantity of an appropriate phosphorus compound in any of the steps preceding calcination, preferably before or during the formation of the gel. The phosphorus compound is preferably selected form organic or inorganic oxygenated compounds, capable of forming phosphorus oxide or a phosphate group after the oxidizing thermal treatment suitable for drying and calcining the gel, more preferably such as to avoid introducing traces of undesirable metals in the matrix of porous oxide obtained after calcination.

Sol-gel methods for the preparation of amorphous silico-aluminas which can be adapted for the purpose are described, for example, in European patent applications EP-A 160,145, EP-A 340,868 and EP-A 659,478 or in the publication "Journal of Catalysis, Vol. 60 (1969), pages 156-166. ~~whose contents are incorporated herein as reference, without limiting the scope of the present invention to said methods.~~

An advantageous preparation method, which forms a second object of the present invention, includes, in a first step (i), the preparation of a mixture comprising a tetraalkyl ammonium hydroxide, having the function of templating agent, an aluminum compound and a silicon compound, which can be hydrolyzed to the corresponding hydrated oxides, an

solid materials in a mixture, for example, according to the methods described in European patent applications EP-A 550,922 and EP-A 665,055, the latter preferred, both filed by the Applicant.~~, whose contents are incorporated herein as reference.~~

In particular, according to a preferred method, the gel obtained from the hydrolysis and gelification of the aqueous mixture of Al alkoxide, tetra-alkyl silicate and oxygenated phosphorus compound, prepared as described above, is mixed, before the calcination step (iii), with the desired quantity of inorganic binder, based on the dry weight, normally with a weight ratio between binder and gel (humid) within the range of 0.05 to 0.5. A plasticizing agent, selected from those generally known to be suitable for the purpose is also preferably added, for example methyl cellulose, stearine, glycerol, more preferably methyl cellulose, to favour the formation of a homogeneous and easily processable paste. This plasticizer is generally added in a quantity ranging from 5 to 20 g per 100 g of binder.

A suitable acidifying compound selected from organic acids, such as acetic acid or acetic anhydride, oxalic acid, or inorganic acids, such as hydrochloric acid or phosphoric acid, is then added in a quantity preferably ranging from 0.5 to 8 g per 100 g of binder. Acetic acid is

hydrocracking and/or hydro-isomerization, a metal having a hydro-dehydrogenating activity when in the presence of hydrogen/hydrocarbon mixtures, is supported on the catalytically active porous solid according to the present invention. Metals especially suitable for the purpose are those of groups 6 to 10 of the periodic table, such as, for example, chromium, iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium, osmium and platinum. Combinations of nickel with molybdenum, tungsten and cobalt as well as the noble metals platinum or palladium, and preferably platinum, are of particular interest.

According to the present invention, the metal should be conveniently distributed as uniformly as possible on the porous surface of the carrier, in order to maximize the catalytically surface which is effectively active. For this purpose, various known methods can be used, such as those described for example in European patent application EP-A 582,347. ~~, whose contents are incorporated herein as reference.~~ In particular, according to the impregnation method, the amorphous porous solid of the present invention, as such or preferably extruded, is put in contact with an aqueous or alcoholic solution of a compound of the desired metal for a period sufficient to provide a homogeneous distribution of the metal in the solid. This normally requires from a few minutes to several hours, preferably under stir-

CLAIMS

1. A catalytically active amorphous porous solid, comprising a mixed oxide of silicon, aluminum and phosphorus, characterized by an atomic ratio Si/Al ranging from 10 to 250, a P/Al ratio of at least 0.1~~, but lower than 5~~ and not higher than 3.5, a total pore volume ranging from 0.5 to 2.0 ml/g, with an average diameter ranging from 3 to 40 nm, and a specific surface area ranging from 200 to 1000 m^2/g.

2. The solid according to claim 1, wherein, in the mixed oxide, said atomic ratio Si/Al ranges from 15 to 200 and said atomic ratio P/Al ranges from 0.3 to 3.5.

3. The solid according to claim 1 or 2, wherein said pore volume ranges from 0.7 to 1.7 ml/g, with an average diameter ranging from 5 to 30 nm, and said surface area ranges from 300 to 900 m^2/g.

4. The solid according to any of the previous claims, wherein the difference between 10% and 90% of the pore dimensions in the distribution curve is within a diameter range of 2 to 40 nm.

5. The solid according to any of the previous claims, comprising at least 95% by weight of said mixed oxide and up to 5% by weight of at least one oxide of a metal selected from Ti, Zr, V, Cr, Fe, Co, Ni, Pt, Pd, Mo, Zn, Ga and Sn.

6. A catalytically active solid composition comprising from 30 to 99% by weight of the amorphous porous solid according to any of the previous claims, and from 70 to 1% by weight of an inert inorganic binder.

7. The composition according to claim 6, comprising from 50 to 80% by weight of said amorphous porous solid and from 50 to 20% by weight of said inert inorganic binder.

8. The composition according to any of the previous claims 6 and 7, wherein said inert binder is selected from silica, alumina, clay, titanium oxide (TiO_2), zirconium oxide (ZrO_2), boron oxide (B_2O_3), or mixtures thereof.

9. The composition according to any of the previous claims from 6 to 8, wherein said inert binder essentially consists of alumina.

10. The composition according to one of the previous claims from 6 to 9, having the form of pellets with a diameter of 2 to 5 mm and a length of 2 to 10 mm.

11. Use of the amorphous porous solid according to any of the previous claims from 1 to 5, or of the composition according to any of the previous claims from 6 to 10, as catalyst or active catalyst carrier in acid-catalyzed industrial processes.

12. Use according to claim 11, in alkylation, isomeriza-

tion processes and in the oligomerization of hydrocarbons.

13. Use according to the previous claim 11 or 12, in processes comprising hydro-dehydrogenation reactions.

14. Use according to claim 13, in hydrocracking, hydroisomerization processes and in the dewaxing of hydrocarbons.

15. A process for the preparation of a porous solid according to any of the previous claims from 1 to 5, comprising the following steps in succession:

(i) preparation of an aqueous mixture comprising a tetra-alkyl ammonium hydroxide, a hydrolyzable aluminum compound, a hydrolyzable silicon compound and an oxygenated compound of phosphorus in such proportions as to have an atomic ratio Si/Al ranging from 10 to 250 and a P/Al atomic ratio ranging of from 0.1 to 3.5 ~~the desired proportions~~, and a sufficient quantity of water to dissolve and hydrolyze said compounds;

(ii) heating of said mixture in an alkaline environment, preferably maintaining the pH at a value greater than 10, and so that there is essentially no exchange of material with the outside, to obtain the formation of a gel;

(iii) drying and calcination of the gel of step

(ii) to obtain the desired amorphous porous solid.

16. The process according to claim 15, wherein said aluminum compound is an aluminum trialkoxide comprising from 1 to 10 carbon atoms in each alkoxide residue, said hydrolyzable silicon compound is a silicate of at least one hydrocarbon residue, preferably a tetraalkylorthosilicate, comprising from 1 to 10 carbon atoms for each alkyl residue, and said oxygenated compound of phosphorus is a phosphoric or a phosphonic salt or ester or the corresponding acid.

17. The process according to claim 16, wherein said phosphorus compound is an ammonium salt or an ester of phosphoric or phosphonic acid in which each alkyl residue comprises from 1 to 10 carbon atoms.

18. The process according to any of the claims from 15 to 17, wherein, in step (I), the following atomic or molar ratios are used: Si/Al from 10/1 to 250/1, tetraalkyl ammonium hydroxide/Si from 0.05/1 to 0.2/1, H_2O/Si from 5/1 to 40/1, P/Al from 0.1 to 5.0

19. The process according to any of the claims from 15 to 18, wherein, in step (i), the mixture is heated to a temperature ranging from 30 to 80°C until a limpid solution is obtained.

20. The process according to any of the claims from 15 to

19, wherein, in step (ii), said heating is effected at a pH ranging from 11 to 12 and to a temperature ranging from 60 to 120°C, operating in a closed vessel at autogenous pressure of the system, or at atmospheric pressure with refluxing, for a time ranging from 10 minutes to 3 hours.

21. The process according to any of the claims from 15 to 20, wherein, in step (ii), an alcohol, having from 1 to 10 carbon atoms, preferably ethanol, is added to the mixture up to an alcohol/Si ratio of 8/1.

22. The process according to any of the claims from 15 to 21, comprising an aging step of the gel of 1 to 24 hours at the end of step (ii) and before the drying and calcination step (iii).

23. A process for the preparation of the solid composition according to any of the previous claims from 6 to 10, comprising the formation of a mixture containing from 30 to 99% by weight of the amorphous porous solid according to any of the previous claims from 1 to 5, and from 70 to 1% by weight of an inert inorganic binder.

24. The process according to claim 23, wherein said porous solid is in the form of a humid gel and is mixed with said binder with a weight ratio between binder and gel ranging from 0.05 to 0.5.

25. The process according to one of the previous claims 23

or 24, wherein said mixture also comprises a plasticizing agent selected from methyl cellulose, stearine and glycerol, preferably methyl cellulose in a quantity ranging from 5 to 20 g per 100 g of binder.

26. The process according to one of the previous claims from 23 to 25, wherein an organic acid is added to said mixture in a quantity ranging from 0.5 to 8 g per 100 g of binder.

27. The process according to one of the previous claims from 23 to 26, wherein said mixture is homogenized by mixing and heating to a temperature ranging from 40 to 90°C, until a paste is obtained, it is then extruded into cylindrical granules having a size of 2-10 mm in length and 0.5-4.0 mm in diameter, and is finally dried and calcined.